A study of surface electronic structures on Pt_3M (M=Ti, V, Cr, Fe, Co, Ni) polycrystalline alloys and Pt_3Ni [100], [110], and [111] single crystals

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Abstract

The tailoring of new materials that can mimic the catalytic properties of Pt has been one of the most challenging tasks in hydrogen fuel cell research. Although no substitutes for Pt have yet been found, Pt is still considered as the best catalyst for fuel cells materials, recent studies in Phil Ross' group in MSD have shown that rate of the oxygen reduction reaction (ORR), $O_2 + 4 H^+ + 4e^- => 2 H_2O$, is improved by factor of 2~3 when the Pt is alloyed with certain $3d$ transition metals. This enhanced activity results in a considerable savings in the amount of Pt required in the fuel cell. However, the reason for the enhanced activity, and the role of the transition metal, which by itself is completely inactive for this reaction, is not understood.

In this presentation, the surface electronic structures of Pt_3M (M = Ti, V, Cr, Fe, Co, Ni) polycrystalline alloys are presented using valence band (VB) photoemission spectroscopy. Upon thermal annealing of the alloys at high temperatures, surface enrichment in Pt is accompanied by changes in the valence band spectra indicating modified electronic structures on these surfaces relative to pure Pt. The measured d-band centers and widths for the annealed alloy surfaces show a good qualitative agreement with theoretical model calculations based on the formation of Pt "skin" layer on the top surface and a subsurface layer enriched in the $3d$ transition metal. Furthermore, Pt_3Ni single crystals with all 3 low-indexes surfaces are studied for the investigation on the structure influences on the modified electronic structures. In the case of Pt_3Ni [100] & [110] crystals, the unique surface reconstructions are also observed with LEED study. The measured electronic structures are discussed together with the DFT theoretical model calculation.